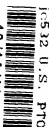


10/14/98



U.S. PTO

Practitioner's Docket No. 50278

PATENT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application  
 Assistant Commissioner for Patents  
 Washington, D.C. 20231



U.S. PTO

## NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): Martin T. Goosey Joachim Buch Rebecca Holland

John E. Graves Mark A. Poole

WARNING: 37 C.F.R. § 1.41(a)(1) points out: Deborah Hirst

\*(a) A patent is applied for in the name or names of the actual inventor or inventors.

“(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(f) is filed supplying or changing the name or names of the inventor or inventors.”

For (title):

ELECTROLESS PLATING PROCESSES

## CERTIFICATION UNDER 37 C.F.R. 1.10\*

(Express Mail label number is mandatory.)

(Express Mail certification is optional.)

I hereby certify that this New Application Transmittal and the documents referred to as attached therein are being deposited with the United States Postal Service on this date October 14, 1998, in an envelope as “Express Mail Post Office to Addressee,” mailing Label Number EE762903733US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

Deanna M. Landry

(type or print name of person mailing paper)

Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

WARNING: Each paper or fee filed by “Express Mail” must have the number of the “Express Mail” mailing label placed thereon prior to mailing, 37 C.F.R. 1.10(b).

“Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will not be granted on petition.” Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

(Application Transmittal [4-1]—page 1 of 11)

## 1. Type of Application

This new application is for a(n)

(check one applicable item below)

- ☒ Original (nonprovisional)  
☐ Design  
☐ Plant

**WARNING:** Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.

**WARNING:** Do not use this transmittal for the filing of a provisional application.

**NOTE:** If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

- ☐ Divisional.  
☐ Continuation.  
☐ Continuation-in-part (C-I-P).

## 2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

**NOTE:** A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. 112. Each prior application must also be:

(i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or

(ii) Complete as set forth in § 1.51(b); or

(iii) Entitled to a filing date as set forth in § 1.53(b) or § 1.53(d) and include the basic filing fee set forth in § 1.16; or

(iv) Entitled to a filing date as set forth in § 1.53(b) and have paid therein the processing and retention fee set forth in § 1.21(f) within the time period set forth in § 1.53(f).

37 C.F.R. § 1.78(a)(1).

**NOTE:** If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an international Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

**WARNING:** If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.

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061101 EEE2168

**WARNING:** When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application must be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).

- ☐ The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

### 3. Papers Enclosed

A. Required for filing date under 37 C.F.R. § 1.53(b) (Regular) or 37 C.F.R. § 1.153 (Design) Application

16 Pages of specification

2 Pages of claims

3 Sheets of drawing

**WARNING:** DO NOT submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 CFR 1.84, see Notice of March 9, 1988 (1990 O.G. 57-62).

**NOTE:** "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page . . ." 37 C.F.R. 1.84(c).

(complete the following, if applicable)

- ☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. 1.84(b).
- ☒ formal
- ☐ informal

### B. Other Papers Enclosed

       Pages of declaration and power of attorney

1 Pages of abstract

       Other

### 4. Additional papers enclosed

- ☐ Amendment to claims
- ☐ Cancel in this applications claims \_\_\_\_\_ before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)
- ☐ Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)
- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement (37 C.F.R. 1.98)
- ☐ Form PTO-1449 (PTO/SB/08A and 08B)
- ☐ Citations

- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other

#### 5. Declaration or oath (including power of attorney)

**NOTE:** A newly executed declaration is not required in a continuation or divisional application provided that the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47, then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. §§ 1.63(d)(1)–(3).

**NOTE:** A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name including family name and at least one given name, without abbreviation together with any other given name or initial, and the residence, post office address and country or citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. § 1.63(a)(1)–(4).

- ☐ Enclosed
- Executed by

(check all applicable boxes)

- ☐ inventor(s).
- ☐ legal representative of inventor(s).  
37 CFR 1.42 or 1.43.
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
- ☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. See item 13 below for fee.

- ☒ Not Enclosed.

**NOTE:** Where the filing is a completion in the U.S. of an International Application or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.

- ☐ Application is made by a person authorized under 37 C.F.R. 1.41(c) on behalf of all the above named inventor(s).

(The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently).

- ☐ Showing that the filing is authorized.  
(not required unless called into question. 37 CFR 1.41(d))

(Application Transmittal [4-1]—page 4 of 11)

## 6. Inventorship Statement

**WARNING:** If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.

The inventorship for all the claims in this application are:

☒ The same.

or

☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

☐ is submitted.

☐ will be submitted.

## 7. Language

**NOTE:** An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of \$130.00 required by 37 CFR 1.17(f) is required to be filed with the application, or within such time as may be set by the Office. 37 CFR 1.52(d).

☒ English

☐ Non-English

☐ The attached translation includes a statement that the translation is accurate. 37 C.F.R. 1.52(d).

## 8. Assignment

☒ An assignment of the invention to Shipley Company, L.L.C. of  
Marlborough, MA 01752

☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☒ will follow.

**NOTE:** "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

**WARNING:** A newly executed "CERTIFICATE UNDER 37 CFR 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.

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# 9. Certified Copy

Certified copy(ies) of application(s)

<b>United Kingdom</b>	<b>9722028.9</b>	<b>October 17, 1997</b>
Country	Appln. No.	Filed
Country	Appln. No.	Filed
Country	Appln. No.	Filed

from which priority is claimed

☐ is (are) attached.

☒ will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

# 10. Fee Calculation (37 C.F.R. 1.16)

A. ☒ Regular application

CLAIMS AS FILED			
Number filed	Number Extra	Rate	Basic Fee 37 C.F.R. 1.16(a) \$790.00
Total Claims (37 CFR 1.16(c)) 13 - 20 =	x	\$ 22.00	
Independent Claims (37 CFR 1.16(b)) 2 - 3 =	x	\$ 82.00	
Multiple dependent claim(s), if any (37 CFR 1.16(d))	+	\$270.00	<b>270.00</b>

☐ Amendment cancelling extra claims is enclosed.

☐ Amendment deleting multiple-dependencies is enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d).

Filing Fee Calculation

**\$ 1,060.00**

B. ☐ Design application  
(\$330.00—37 CFR 1.16(f))

Filing Fee Calculation

\$ \_\_\_\_\_

C. ☐ Plant application  
(\$540.00—37 CFR 1.16(g))

Filing fee calculation

\$ \_\_\_\_\_

11. Small Entity Statement(s)

- ☐ Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is (are) attached.

**WARNING:** "Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under § 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under § 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this section." 37 C.F.R. § 1.28(a)(2).

(complete the following, if applicable)

- ☐ Status as a small entity was claimed in prior application \_\_\_\_\_ / \_\_\_\_\_, filed on \_\_\_\_\_, from which benefit is being claimed for this application under:

35 U.S.C. ☐ 119(e),  
☐ 120,  
☐ 121,  
☐ 365(c).

and which status as a small entity is still proper and desired.

- ☐ A copy of the statement in the prior application is included.

Filing Fee Calculation (50% of A, B or C above)

\$ \_\_\_\_\_

NOTE: Any excess of the full fee paid will be refunded if small entity status is established and a refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under § 1.136. 37 CFR 1.28(a).

12. Request for International-Type Search (37 C.F.R. 1.104(d))

(complete, if applicable)

- ☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

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13. Fee Payment Being Made at This Time

- ☐ Not Enclosed
- ☐ No filing fee is to be paid at this time.  
(This and the surcharge required by 37 C.F.R. 1.16(e) can be paid subsequently.)
- ☒ Enclosed
- ☒ Filing fee \$ 1,060.00
- ☐ Recording assignment  
(\$40.00; 37 C.F.R. 1.21(h))  
(See attached "COVER SHEET FOR  
ASSIGNMENT ACCOMPANYING NEW  
APPLICATION".) \$ \_\_\_\_\_
- ☐ Petition fee for filing by other than all the  
inventors or person on behalf of the inventor  
where inventor refused to sign or cannot be  
reached  
(\$130.00; 37 C.F.R. 1.47 and 1.17(i)) \$ \_\_\_\_\_
- ☐ For processing an application with a  
specification in  
a non-English language  
(\$130.00; 37 C.F.R. 1.52(d) and 1.17(k)) \$ \_\_\_\_\_
- ☐ Processing and retention fee  
(\$130.00; 37 C.F.R. 1.53(d) and 1.21(l)) \$ \_\_\_\_\_
- ☐ Fee for international-type search report  
(\$40.00; 37 C.F.R. 1.21(e)) \$ \_\_\_\_\_

NOTE: 37 CFR 1.21(f) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 CFR 1.53(f) and this, as well as the changes to 37 CFR 1.53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1.21(f) must be paid, within 1 year from notification under § 53(f).

Total fees enclosed

\$ 1,060.00

14. Method of Payment of Fees

- ☒ Check in the amount of \$ 1,060.00
- ☐ Charge Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).

(Application Transmittal [4-1]—page 8 of 11)

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## 15. Authorization to Charge Additional Fees

**WARNING:** If no fees are to be paid on filing, the following items should not be completed.

**WARNING:** Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

- ☒ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 04-1105:

- ☒ 37 C.F.R. 1.16(a), (f) or (g) (filing fees)  
☐ 37 C.F.R. 1.16(b), (c) and (d) (presentation of extra claims)

**NOTE:** Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

- ☒ 37 C.F.R. 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)  
☐ 37 C.F.R. §§ 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a)).  
☒ 37 C.F.R. 1.17 (application processing fees)

**NOTE:** "... A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).

- ☐ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

**NOTE:** Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).

**NOTE:** 37 CFR 1.28(b) requires "Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . the issue fee. . . ." From the wording of 37 CFR 1.28(b), (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

**16. Instructions as to Overpayment**

NOTE: "... Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).


- ☒ Credit Account No. 04-1105  
☐ Refund

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Reg. No. 33,860

Tel. No. ( 508 ) 485-7772

Customer No.

  
\_\_\_\_\_  
SIGNATURE OF PRACTITIONER

Peter F. Corless

(type or print name of attorney)

P.O. Box 556

P.O. Address

Marlborough, MA 01752

☐ **Incorporation by reference of added pages**

*(check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)*

- ☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added \_\_\_\_\_

- ☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added \_\_\_\_\_

- ☐ Plus added pages deleting names of inventor(s) named in prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added \_\_\_\_\_

- ☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added \_\_\_\_\_

☒ **Statement Where No Further Pages Added**

*(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)*

- ☒ This transmittal ends with this page.

## ELECTROLESS PLATING PROCESSES

## BACKGROUND

## 1. Field of the Invention

This invention relates to metallization processes and more particularly to electroless plating, including e.g., copper plating of certain polymers such as ABS (acrylonitrile butadiene styrene) copolymers, epoxy resins, and other organic polymers, including non carbon-fluorine bond polymers.

## 2. Background

Conventional methods employed for metallizing polymers (e.g., ABS) utilize aggressive oxidizing agents such as chromic acid as part of the surface treatment prior to conditioning, catalyzation and electroless metal deposition. This results in a lengthy process which often utilizes undesirable chemicals that are both unpleasant to handle, difficult to treat after use and which are becoming increasingly environmentally unacceptable.

## SUMMARY OF THE INVENTION

We have now found processes that include a surface treatment providing a substrate morphology leading, after further steps, to direct catalyzation of the substrate surface without the need for the traditional subsequent neutralization, conditioning and tin/palladium catalyzation steps. This is a major improvement since it removes several process steps, one of which is the use of chromic acid. The invention also obviates the need to use an expensive palladium based plating catalyst. The new processes are, in part, based upon the use of electrochemically or otherwise generated metal ions (e.g.  $\text{Ag}^{2+}$  or  $\text{Co}^{3+}$ ), referred to herein as metal activators. Suitable metal activators include silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium, and vanadium, with silver and cobalt being generally preferred.

In use, the metal activators are oxidized to a higher state (e.g. to Ag (II) or to Co (III)), preferably electrochemically. Without being bound by theory, it is believed the oxidized metal activator generates reactive hydroxyl species from water, such as hydroxyl radicals. These hydroxyl species are very reactive and attack polymer surfaces, particularly organic polymers, to give an ideal pitted morphology deemed desirable for subsequent metal adhesion and which is similar to that provided by chromic acid. In this process, following surface texturing the

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substrate is immersed in a reducing agent pre-dip solution and it can then be plated immediately by immersion in an electroless metal plating solution, e.g., copper bath without any further process steps. A further advantage of the invention is that the metal activator treatment solution (e.g. silver or cobalt solution) may be regenerated such as by electrochemical methods thus reducing problems encountered with waste treatment.

The present invention provides improved methods of plating polymers with metal e.g., copper, silver, nickel, gold, tin, cobalt etc. for subsequent use in other applications where molded plastic parts are used, e.g. to produce decorative parts such as in perfume bottle tops and in decorative automobile parts, and for electromagnetic interference (EMI) shielding applications. The invention is also useful to plate parts to produce molded electrical interconnect devices.

The present invention also is particularly useful in the manufacture of printed circuit boards. For example oxidizing agents such as potassium permanganate are used to remove resin smear and to provide a textured polymer surface prior to conditioning, catalyzation and electroless metal deposition. The use of transition oxidized metal species (e.g.  $\text{Ag}^{2+}$  or  $\text{Co}^{3+}$ ) in the production process removes several process steps and reduces chemical consumption.

As used herein, the term "metal activator" refers to a metal that is sufficiently water soluble to function in the processes of the invention and can be oxidized to a higher state to generate reactive hydroxyl species (e.g. hydroxide radicals) from water and promote electroless plating in accordance with the processes of the invention. Thus, suitable metal activators can be identified by simple testing, e.g. by testing a particular metal by the general procedure of Example 1 which follows to determine if electroless deposition is provided. In any event, as mentioned above, suitable metal activators include silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium, and vanadium, with silver and cobalt being generally preferred.

Other aspects of the invention are disclosed infra.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates diagrammatically a preferred process of the invention.

FIG. 2 shows a preferred additive process of the invention.

FIG. 3 shows a preferred pattern plate process of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

According to the first aspect of the invention, a process is provided for metallizing a part, particularly a polymer substrate such as ABS, which has been etched by a reactive hydroxyl species (e.g. hydroxyl radicals) generated from water as a result of the presence a metal activator (e.g.  $\text{Ag}^{2+}$ ,  $\text{Co}^{3+}$ ) in the water, and applying a reducing agent capable of reducing the oxidized metal activator species to a lower oxidation state (e.g. a zero oxidation state, or  $\text{Ag}^{2+}$  to  $\text{Ag}^+$ , or  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ ). Any of a wide variety of reducing agents may be employed, e.g., a boron reagent such as a boron hydride or salts thereof e.g. sodium borohydride, and other boranes such as dimethylaminoborane; and other agents such as sodium dithionite, formaldehyde or a phosphite e.g., sodium hypophosphite, which is preferred. The oxidized metal activator species is typically generated electrochemically. After application of the reducing agent, electroless plating is employed, e.g., using electroless copper, nickel and the like to form a metal surface on the polymer substrate. In contrast to prior electroless processes, a Pd/tin, palladium, platinum or other electroless catalyst need not be employed to deposit effectively an electroless metal layer. In addition to ABS, other preferred polymers for metallization include e.g. polyamide, polycarbonate, ABS/polycarbonate blends, epoxy laminates particularly as used in printed circuit board manufacture, polyetherimides and liquid crystal polymers.

As another aspect of this invention, methods are provided for plating electroless metal such as electroless copper on a part, particularly a polymer substrate such as ABS, which comprises forming a metal layer on ABS having silver, cobalt or other metal activator thereon.

As yet a further aspect of this invention there is disclosed the use of electrochemically generated metal activator ions or oxidized species, such as silver<sup>2+</sup> ions,  $\text{Co}^{3+}$ , cerium (III) or (IV), iron (II) or (III), manganese (IV) or higher, nickel (II) (II) or (IV), ruthenium (V) (VI) (VII) (VIII), vanadium (IV) or (V), etc., in a combined surface treatment and metallization process

where e.g. the silver ions generate hydroxyl radicals capable of texturing the polymer surface and which can also be reduced to silver metal on the surface so that the silver metal catalyses the subsequent electroless metal to be deposited thereon from a bath thereof, e.g. copper.

In order to achieve good quality metal deposits on polymers such as ABS, their surfaces are normally textured using aggressive solutions that provide a chemically and physically modified surface that is optimized for subsequent conditioning and electroless plating processes. Such materials that have been employed typically are strong oxidizing agents such as the alkali permanganates used with thermosets such as epoxides and chromic acid as used with thermoplastics such as Acrylonitrile Butadiene Styrene (ABS). The aim is to produce a reticulated textured surface that not only is amenable to conditioning with a subsequent surfactant but which also provides good keying and mechanical adhesion of the subsequently deposited electroless copper or other metal.

In the case of prior use of ABS and chromic acid, the acid preferentially attacks ABS butadiene groups leaving a surface optimized for subsequent plating. Unfortunately, chromic acid may be a carcinogen and also presents various waste treatment, disposal problems and environmental concerns. Accordingly, there is great interest therefore in the development of alternative methods of metallization that do not utilize chromic acid. The present invention provides such methods.

Oxidized metal activator species preferably are generated electrochemically using an undivided or divided cell containing the metal activator typically in salt form, e.g. as a sulphate salt in aqueous sulphuric acid solution, a nitrate salt in aqueous nitric acid solution, a fluoroborate salt in aqueous fluoroboric acid solution, a perchlorate salt in aqueous perchloric acid solution, a fluoride salt in aqueous hydrofluoric acid solution, a chloride salt in aqueous hydrochloric acid solution, a bromide salt in aqueous hydrobromic acid solution, a phosphate salt in aqueous phosphoric acid solution, a nitrate salt dissolved in either trifluoromethane sulphonic acid or trifluoroacetic acid aqueous solution, etc., or from a mixture of the above mentioned salts and acids. Specifically preferred metal salts/acid combinations include silver nitrate/nitric acid; silver percholate/perchloric acid; silver sulphate/sulphuric acid; silver phosphate/phosphoric

acid; silver nitrate/trifluoromethane sulphonic acid; silver nitrate/trifluoroacetic acid; cobalt sulphate/sulphuric acid; and the like. Other suitable cobalt salts and acid combinations include halides, sulphates, nitrates and tetrafluoroborates dissolved in sulphuric, nitric, tetrafluoroboric or phosphoric acid, or any combination thereof. Ruthenium (IV) oxide and sodium metavanadate also may be employed dissolved in any mixture of the above mentioned acids. Other suitable metal activator salts include cerium (III) sulphate, iron (II) sulphate, manganese (II) sulphate, nickel (II) sulphate, dissolved in any of the above acids.

Additionally, a mixture of different metal activators may be used in a single process.

Using an inert electrode such as platinum, platinized titanium, platinum on niobium or tantalum, ruthenium or iridium dioxide on titanium, or carbon (glassy or vitreous) and a current density of 1 mA/cm<sup>2</sup> to 10 A/cm<sup>2</sup> with 500mA/cm<sup>2</sup> being preferred for ABS, the oxidized metal activator species (e.g. Ag<sup>2+</sup> or Co<sup>3+</sup>) form rapidly and can readily attack polymers such as ABS giving a nicely textured surface virtually identical to that produced with chromic acid. Subsequent processing with a reducing agent and electroless metal plating solution e.g., copper plating gives electroless copper deposits with adhesion values equal to or better than those from substrates metallized following conventional chromic acid treatment. Oxidized cobalt species can be generated without a divided electrochemical cell, providing further cost reductions and easier processing.

The oxidized metal activator species can be generated by methods other than electrochemical reaction. For example, silver<sup>2+</sup> ions can be generated chemically from solutions of silver<sup>+1</sup> ions by oxidation with strong oxidizing agents such as ozone or by dissolution of silver (II) oxide, silver (II) fluoride or silver (II) fluorosulphate in acid. Other oxidized metal activators also can be generated chemically, rather than electrochemically. However, for ease of processing, electrochemical regeneration is generally preferred.

Regardless of how the oxidized metal activator species or ions are generated, it is desirable to use the oxidized species in the form of an aqueous solution where the oxidized species are present in a concentration of from 0.01 moles to 2.0 moles and preferably, in a



concentration of from 0.1 to 1 mole per liter of treatment solution. The actual preferred concentration is dependent upon the substrate to be treated, which concentration can be readily determined empirically based on the present disclosure. The higher concentrations are generally more active. ABS is readily etched and a lower concentration solution of the metal activator ions in solution would be used to treat ABS than, for example, epoxy where a higher concentration of the oxidized activator in solution would be required.

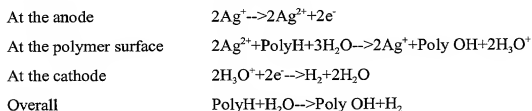
As discussed above, if the part to be plated, e.g. a polymer part such as an ABS part, is treated with the metal activator and subsequently immersed in a solution of a reducing agent such as a phosphite such as sodium hypophosphite; or a thionite such as sodium dithionite; or formaldehyde; or a hydride such as sodium borohydride; or a borane such as dimethylaminoborane (DMAB), the reduced metal activator (e.g. silver, cobalt, etc.) remains and the ABS or other part can be immediately plated with electroless metal e.g., copper without any further conditioning or catalyzation steps. The reducing solution contains sufficient reducing agent to reduce at least a portion of the oxidized metal activator. For this reason, the concentration of the reducing agent is dependent upon its ability to reduce the oxidized metal activator. Strong reducing agents may be used in lower concentration. Typically, the reducing agent is present in a molar ratio of from 0.1 to 2.5 times the concentration of the metal activator and preferably, in a ratio of from 0.2 to 1.2 times the concentration of the metal activator.

It is an important aspect of the invention that the oxidized metal activator, such as  $\text{Ag}^{2+}$ ,  $\text{Co}^{3+}$ , cerium (IV), iron (III), manganese (IV), nickel (III), ruthenium (V), rhodium (IV), metavanadate, etc. species, may be continuously regenerated. Therefore, the total loss of metal couple is small offsetting the cost of the relatively expensive metal couple salts. By continuous regeneration, though some metal loss will occur due to dry-out and uncharacterized side reactions, the overall loss is minimal. Regeneration may be easily conducted, e.g. by subjecting the solution after exposure to a part to be plated to further electrochemical treatment to regenerate higher oxidization state metal species. Even more preferably, regeneration is continually conducted during exposure of parts to provide a more or less steady state of oxidized metal activator species.

As a preferred embodiment of this invention oxidized metal activator species, which may be e.g. electrochemically generated  $\text{Ag}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Co}^{3+}$  ions or species are employed in a combined surface treatment and metallization process where the oxidized metal activator species ions generate reactive hydroxyl species (e.g. hydroxyl radicals) capable of texturizing the polymer surface and which can also be reduced to a lower oxidation state metal activator (e.g. silver metal or cobalt metal) on the surface so that the reduced metal catalyzes the subsequent electroless metal to be deposited thereon from a bath thereof, e.g., copper, nickel, etc.

Silver ions normally exist in solution as the single charged  $\text{Ag}^+$  ion, as is typically found for example in solutions of silver (I) nitrate, silver (I) tetrafluoroborate, silver (I) perchlorate and silver (I) fluoride. However, under certain conditions silver can be oxidized further to the doubly charged  $\text{Ag}^{2+}$  ion or species. This ion is very reactive and can be used to attack virtually all organic materials including polymers. The  $\text{Ag}^{2+}$  ion in solution is not stable and through a series of reactions converts back to  $\text{Ag}^+$ , typically over a period of a few days. However, the reversion of  $\text{Ag}^{2+}$  to  $\text{Ag}^+$  leads to the generation of hydroxyl radicals and it is this species that is so aggressive towards organic chemical bonds.

The major reaction steps resulting in the surface treatment are not fully understood but are generally described by the following mechanism where PolyH and Poly OH represent the untreated and treated polymer surfaces, respectively.



The room temperature process requires only the consumption of electricity and water, and the only by-product is hydrogen. The latter point represents a significant improvement over the other "wet" treatments which require the disposal of toxic materials. Furthermore, any organic or biological matter present is oxidized to produce carbon dioxide and water. The mechanism outlined above clearly should not be considered as being definitive: in particular, it is quite likely that further oxidation takes place, possibly involving the formation of carbonyl surface groups.

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The temperature of various solutions used in the processes of the invention may suitably vary through a wide range. Some preferred temperatures are set forth in the examples which follow. For instance, a plastic such as an ABS or epoxy substrate, may be first treated with a conditioner solution that is above room temperature, e.g. from about 30 to 50°C, more preferably about 35 to 45°C. The part then may be treated with the oxidized metal activator solution that also is preferably above room temperature, e.g. from about 30 to 80°C, more preferably about 40 to 50 or 60°C. The part is then exposed to a reducing agent, which again preferably is at a temperature above room temperature, e.g. from about 25 to 50°C, more preferably about 28 to 35°C. Electroless plating may be conducted at electaed temperatures at is known, e.g. from about 40 to 50°C.

Parts may be exposed to such treatment solutions by immersion, although spray applications also could be employed, at least for some treatments.

The copper deposits formed using processes of the invention have excellent appearance and adhesion. The processes of the invention can replace several steps in the conventional chromic acid based process and in particular it removes the need for an expensive tin/palladium catalyst stage. Although without desiring to be bound to the theory as to what is occurring as a result of using the reducing agent, it is believed that the reducing agent acts to reduce residual metal activator (e.g. silver ions) on the polymer substrate to ground state metal (e.g. silver metal) which is then able to catalyze the electroless copper reaction.

After application of the electroless copper to the polymer substrate, the copper may then be electroplated using conventional technology if desired. It has also been found as another aspect of the invention that applying a solvent swelling system on the substrate prior to etching as taught herein improves the adhesion of the metal to the polymer substrate. For example, solvents such as propylene carbonate, butyrolactone or combinations thereof or methyl ethyl ketone are representative of solvent swelling agents which soften and then swell the polymer surface. A Shipley conditioner product known as PM-920 is useful for this purpose. Also see

U.S. Patent No. 5,178,956 regarding conditioners used prior to etching using etchants other than those described herein.

Commercially available electroless plating compositions can be employed in the processes of the invention. For example, the Shipley Company (Marlborough, MA, USA) has suitable solutions. Shipley's C3000 Electroless Copper is a preferred plating solution. Suitable electroless plating solutions and the use thereof also are widely described in the literature. See, for example, Coombs, *Printed Circuits Handbook*, (3<sup>rd</sup> Edition, McGraw Hill), which is incorporated herein in its entirety. See also U.S. Patent 4,515,829 to Deckert et al., incorporated herein by reference. See also Shipley's U.S. Patent 4,539,044; 3,765,936; and 3,661,597, all incorporated herein by reference.

Silver<sup>2+</sup> (II) was used to treat waste matter (See EP 2 977 738 and U.S. Patent Nos. 4,874,485 and 4,925,643). Also see the paper (3 pages) provided at Science Open Meeting in London, U.K. on May 7, 1997 entitled "New Pretreatments for Polymers", D.M. Brewis, R.H. Dahm and I. Matheson, for the use of silver II and the generation thereof and the one page paper provided at the 1996 Swiss Bonding Meeting entitled, "A New General Method for the Pretreatment of Polymers".

Referring now to the Drawings, FIG. 1 diagrammatically illustrates the etching of the plastic substrate. In FIG. 1, there is shown a container 10 which is divided by a cation exchange membrane 11, e.g., DUPONT NAFION-fluoro polymer cation exchange membrane. At 12, there is shown a platinised-titanium mesh electrode (cathode) coupled to the negative terminal of a direct current (d.c.) source. An anode 13 of platinised-titanium mesh electrode is connected to the positive terminal +Ve of the d.c. source.

Between the membrane and the anode 13 there is positioned the plastic substrate, e.g., ABS in the shape of a plaque which is to be etched and which is attached to a holder 14A for moving it into and out of the liquid bath 15.

Agitation is provided by a magnetic stirrer (not shown).

FIG. 2 diagrammatically illustrates a preferred additive process of the invention to plate a printed circuit board, including the through holes. In Step 1 of that process, a printed circuit board substrate 10 having through holes 12 is provided. That substrate 10 may be a laminate material formed from ABS, polyamide, polycarbonate, polyetherimides, epoxies, etc., and blends thereof. In Step 2, the surface of substrate 10 is exposed to an oxidized metal activator, e.g., oxidized silver, cobalt or the like wherein the oxidized species may have been suitably generated electrochemically, as described above with respect to FIG. 1. In that Step 2, the substrate 10 is then exposed to a reducing agent, e.g. a borane, preferably to leave a metal 14 (e.g. Ag if oxidized Ag used as the metal activator) on the substrate. In Step 3, a photoresist 16 then is applied to the planar surfaces and exposed and developed to provide desired bared substrate areas 18. The photoresist may be a dry film or applied as a liquid resist. In Step 4, the treated substrate 10 is immersed or other treated in an electroless plating solution to provide additive electroless metal layers 20, which typically will be electroless copper layer. In Step 5, photoresist 16 is stripped using suitable materials, e.g. a commercial resist stripper solution, which often will be an alkali solution. In Step 6, an etch may be employed if desired to remove any reduced metal activator 14 on the non-plated surfaces of substrate 10.

FIG. 3 diagrammatically illustrates a preferred pattern plate process of the invention to plate a printed circuit board, including through holes thereof. Steps 1 and 2 are the same as described above with respect to FIG. 2. Thus, in Step 1 of the process of FIG. 3, a printed circuit board substrate 40 having through holes 42 is provided. That substrate 40 again may be a laminate material formed from ABS, polyamide, polycarbonate, polyetherimides, epoxy resin, etc., and blends thereof. In Step 2, the surface of substrate 40 is exposed to an oxidized metal activator, e.g., oxidized silver, cobalt or the like wherein the oxidized species may have been suitably generated electrochemically, as described above with respect to FIG. 1. In that Step 2, the substrate 40 is then exposed to a reducing agent, e.g. a borane, preferably to leave a metal 44 (e.g. Ag if oxidized Ag used as the metal activator) on the substrate. In Step 3, the treated substrate 40 is immersed or other treated in an electroless plating solution to provide an electroless metal layer 46, which typically will be an electroless copper layer. In Step 4, a photoresist 48 then is applied to the planar substrate surfaces and exposed and developed to

provide desired bared electrolessly plated substrate areas 50. The photoresist may be a dry film or applied as a liquid resist. In Step 5, the treated substrate 10 is electroplated, e.g. with copper or other metal to provide electrolytic metal layers 52. In Step 6, photoresist 48 is stripped using suitable materials, e.g. a commercial resist stripper solution, which may be an alkali solution. In Step 7, an etch may be employed to remove exposed electroless layer 46.

The following non-limiting examples are illustrative of the invention. The preferred process for metallizing plastics such as ABS, epoxy laminates and the like include the following steps showing ingredient, amounts, temperature conditions and time (expressed as minutes or MINS).

EXAMPLE 1 - Metallization of ABS

<u>PROCESS STEPS</u>	<u>MAKE UP</u>	<u>TEMP/°C</u>	<u>TIME-MINS</u>
1. Apply PM 920 Conditioner <sup>1</sup> to ABS substrate	180 - 250 ml/l	38	1
Rinse (cold water)			2
2. Ag <sup>2+</sup> Etch	4M/l HNO <sub>3</sub> + 1 M/l AgNO <sub>3</sub> i=0.5 A/cm <sup>2</sup>	50	14
Rinse (cold water)			2
3. Apply reducing agent Sodium borohydride	5 g/l	30	1
Rinse (cold water)			2
4. Plate with Cuposit 251 Electroless Copper <sup>1</sup>		46	15
Rinse (cold water)		Room	90

	Temperature	
5. Apply 10% H <sub>2</sub> SO <sub>4</sub> dip	Room Temperature	2
6. Electroplate with Electroposit 1200 Copper <sup>1</sup>	Room Temperature	90
Rinse (cold water)	Room Temperature	
7. Bake	70	60
1. Available from Shipley Company, L.L.C. of Marlboro, Massachusetts, United States of America		

#### EXAMPLE 2 - Metallization of ABS

<u>PROCESS STEPS</u>	<u>TEMP/°C</u>	<u>TIME/MINS</u>
1. Apply PM920 Conditioner to ABS substrate	38	1
Rinse (Cold Water)		2
2. Ag <sup>2+</sup> Etch (having a make-up the same as the Ag <sup>2+</sup> etch of Example 1 above)	50	14
Rinse (Cold Water)		2
3. Apply 10 g/l Sodium Hypophosphite + 35 ml/l sodium hydroxide i=0.5A/cm <sup>2</sup>	25	1
Rinse (Cold Water)		2

4. Plate with Cuposit 251 Electroless Copper	46	15
Rinse (Cold Water)		2
5. Apply 10% H <sub>2</sub> SO <sub>4</sub> dip	Room Temperature	1
6. Electroplate with Electroposit 1200 Copper	Room Temperature	90
Rinse (Cold Water)		2
7. Bake	70	60

### EXAMPLE 3 - Metallization of FR4 Epoxy Circuit Board Substrate

<u>PROCESS STEPS</u>	<u>MAKE UP</u>	<u>TEMP/°C</u>	<u>TIME-MINS</u>
1. Apply Circuposit Hole prep	200 ml/l	75	20
4125 (Shipley) to FR4 epoxy			2
Rinse (cold water)			
2. Ag <sup>2+</sup> Etch	4M/l HNO <sub>3</sub> + 0.5 M/l AgNO <sub>3</sub> i=0.39 A/cm <sup>2</sup>	25 or 50	30 or 15
Rinse (cold water)			2
3. Apply reducing agent	20 g/l	25	1
Sodium borohydride			
Rinse (cold water)			2



4. Plate with Cuposit 251	46	15
Electroless Copper <sup>1</sup>		
Rinse (cold water)		90

1. Available from Shipley Company, L.L.C. of Marlboro, Massachusetts, United States of America

EXAMPLE 4 - Metallization of Photoimageable Dielectric

<u>PROCESS STEPS</u>	<u>MAKE UP</u>	<u>TEMP/°C</u>	<u>TIME-MINS</u>
1. Apply Circuposit Hole prep 4125 to CIBA epoxy-based dielectric layer	200 ml/l	75	20
Rinse (cold water)			2
2. Ag <sup>2+</sup> Etch	4M/l HBF <sub>4</sub> + 1 M/l AgBF <sub>4</sub> i=0.5 A/cm <sup>2</sup>	50	20
Rinse (cold water)			2
3. Apply reducing agent Sodium Hypophosphite + 35 ml/l Cuposit Z (Shipley)	20 g/l	25	1
Rinse (cold water)			2
4. Plate with Cuposit 251		46	15

# Electroless Copper<sup>1</sup>

Rinse (cold water)		2
5. Apply 10% H <sub>2</sub> SO <sub>4</sub> dip	RT	1
6. Electroplate with Electroposit 1200 Copper (Shipley)	RT	90
Rinse (cold water)		2
7. Bake	120	60

1. Available from Shipley Company, L.L.C. of Marlboro, Massachusetts, United States of America

## EXAMPLE 5 – Metallization of ABS

Process Step	Make-up	Temperature (° C)	Time (mins)
PM920 conditioner <sup>1</sup>		38	1
1. Cold water rinse of ABS substrate			2
2. Apply 3302 conditioner <sup>1</sup> to part		60	5
3. Cobalt etch	0.1 M CoSO <sub>4</sub> /2.4 M H <sub>3</sub> PO <sub>4</sub>	35	30
4. Cold water rinse			2
5. Reducing agent	DMAB 80 g/l	25	15
6. Cold water rinse			2
7. Copper bath	Shipley Circuposit 3361 <sup>1</sup>	52	30
8. Cold water rinse			2

1. Available from Shipley Company, L.L.C. of Marlboro, Massachusetts, United States of America

It should be clear that the above process amounts, times, ingredients and etc. may be modified without departing from the invention.

It should also be understood that this process is applicable to polymers other than ABS with exception that in the case of using silver as the metal activator, polymers having carbon-fluorine bonds are preferred. The processes of the invention are useful for metallization of a wide variety of organic resin, including e.g. metallization of polyetherimides for use in metallization of molded electrical interconnect devices. The process also has application in the metallization of polymers for electromagnetic energy shielding.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the spirit or scope of the invention as set forth in the following claims.

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What is claimed is:

1. A process for metal deposition, said process comprising providing an aqueous solution comprising a metal activator, contacting a part to be plated with the aqueous solution of the metal activator for a time sufficient for the metal activator to adsorb onto the part, contacting the part with a reducing agent capable of reducing the metal activator to a lower oxidation state, and metal plating the part by contact with a plating solution.
2. A process for electroless metal deposition of an organic resin part, comprising etching the part with reactive hydroxyl species while catalyzing the part with an electroless metal plating catalyst, and metal plating the part by contacting the part with an electroless metal plating solution.
3. The process of claim 2 the reactive hydroxyl species are generated by reaction with a metal activator.
4. A process of claim 1 or 3 wherein metal activator is silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium, or vanadium.
5. A process of claim 1 or 3 wherein the metal activator is silver.
6. A process of claim 1 or 3 wherein the metal activator is cobalt.
7. A process of any one of claims 1 through 6 where the part to be plated is an organic plastic, preferably acrylonitrile butadiene styrene, polyamide, epoxy, polycarbonate, polyetherimide, or blends thereof.
8. A process of any one of claims 1 through 7 wherein the part to be plated is a printed circuit board substrate or an EMI substrate.

9. A process of any one of claims 1 through claim 8 where the metal activator is present in a concentration of from about 0.01 to 2.0 moles per liter of solution, preferably in a concentration of from about 0.1 to 1 mole per liter of solution.

10. A process of claim 1 where the reducing agent is selected from the group consisting of a phosphite, a hydride, a borane, a borohydride, formaldehyde or a thionite.

11. A process of claim 1 where the plating solution is an electroless copper plating solution.

12. A process of any one of claims 1 or 3 through 11 wherein the metal activator is oxidized electrochemically and the solution containing the oxidized metal substrate is exposed to the part, and the metal activator is reduced.

13. The process of any of the preceding claims wherein a plating catalyst such as Pd/tin, Pd, or platinum separate from the metal activator is not employed, and/or chromic acid or permanganate treatment of the part is not employed.

## ABSTRACT

The invention includes processes for combined polymer surface treatment and metal deposition. Processes of the invention include forming an aqueous solution containing a metal activator, such as an oxidized species of silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium, or vanadium. The activator can be suitably oxidized to a higher oxidation state electrochemically. Exposing a part to be plated (such as an organic resin, e.g. a printed circuit board substrate) to the solution enables reactive hydroxyl species (e.g. hydroxyl radicals) to be generated and to texture the polymer surface. Such texturing facilitates good plated metal adhesion. As part of this contacting process sufficient time is allowed for both surface texturing to take place and for the oxidized metal activator to adsorb onto said part. The part is then contacted with a reducing agent capable of reducing the metal activator to a lower ionic form, or a lower oxidation state. That reduction can result in the formation of metallic catalytic material over the surface of the part. The reduced metal activator can then function to catalyze the electroless deposition of metal such as copper from solution by contacting the part with the plating solution.

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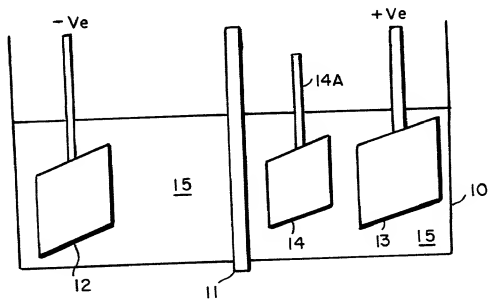
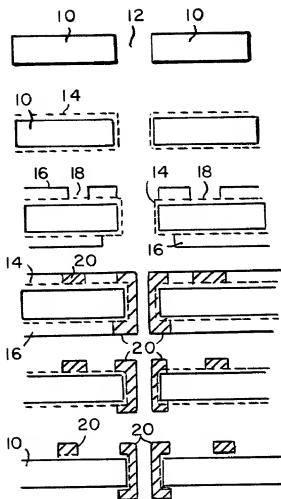


FIG. 1

# FIG. 2

## ADDITIVE PROCESS



STEP 1  
DRILLED UNCLAD LAMINATE

STEP 2  
ETCH AND CATALYSE

STEP 3  
PRINT AND DEVELOP

STEP 4  
FULLY ADDITIVE  
ELECTROLESS COPPER

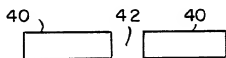
STEP 5  
RESIST STRIP

STEP 6  
OPTIONAL  
LIGHT ETCH TO REMOVE  
METAL ACTIV. RESIDUES

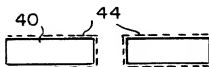


# FIG.3

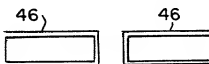
## PATTERN PLATE PROCESS



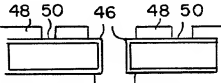
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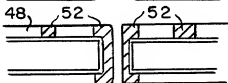
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ETCH AND CATALYSE



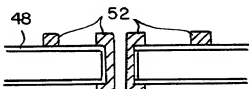
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ELECTROLESS COPPER



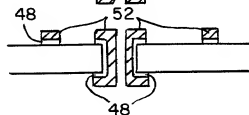
STEP 4  
PRINT AND DEVELOP



STEP 5  
ELECTROPLATE



STEP 6  
RESIST STRIP



STEP 7  
LIGHT  
ETCH